

AD-A141 546

ORGANOSILANE POLYMERS V HYDROSILYL-MODIFIED
POLYCARBOSILANE PRECURSORS FO..(U) UNION CARBIDE CORP
TARRYTOWN NY C L SCHILLING ET AL. SEP 83 TR-83-1

1/1

UNCLASSIFIED

N00014-81-C-0682

F/G 7/3

NL

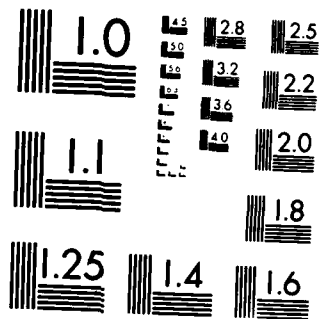
END

DATE

FILED

7 84

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A141 546

DTIC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 83-1	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Organosilane Polymers, V Hydrosilyl-modified Polycarbosilane Precursors for Silicon Carbide		5. TYPE OF REPORT & PERIOD COVERED Technical
7. AUTHOR(s) C. L. Schilling, Jr. and T. C. Williams		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Union Carbide Corporation Tarrytown, N. Y., 10591		8. CONTRACT OR GRANT NUMBER(s) N00014-81-C-0682
11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Branch Office of Naval Research Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE September 1983
		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Technical Report Distribution List This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES To be presented in part at the 1984 Spring Meeting of the American Chemical Society.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Silanes Polycarbosilanes Copolymer Organopolysilanes		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The use of MeSiHCl_2 as a comonomer in the preparation of polycarbosilanes has provided materials with improved pyrolytic yields of silicon carbide ceramic compositions. These polymers, prepared by potassium metal dechlorin- ation of mixtures of chlorosilane monomers in tetrahydrofuran, incorporate MeSiHCl_2 both as trifunctional MeSi units and as difunctional $-\text{MeSiH}-$ units. $\text{MeSi}(3-)$		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 83 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

84 05 29 039

OFFICE OF NAVAL RESEARCH
CONTRACT N00014-81-C-0682
TECHNICAL REPORT 83-1

ORGANOSILANE POLYMERS, V:

HYDROSILYL-MODIFIED POLYCARBOSILANE

PRECURSORS FOR SILICON CARBIDE

by

C. L. Schilling Jr. and T. C. Williams

Union Carbide Corporation
Tarrytown, New York 10591

Reproduction in whole or in part is permitted
for any purpose of the United States Government

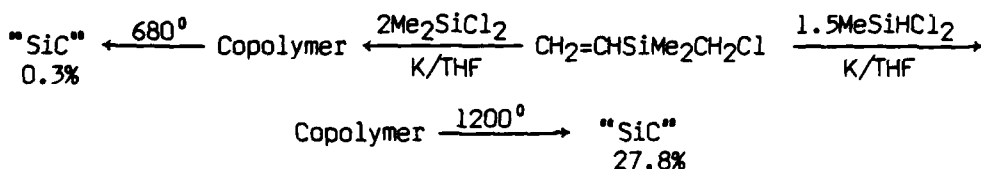
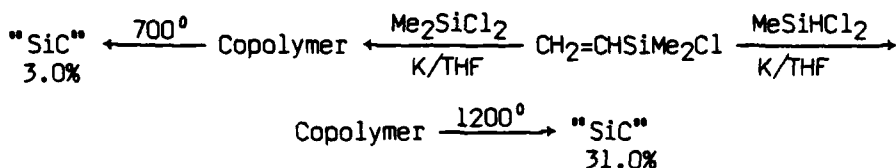
This document has been approved for public
release and sale; its distribution is unlimited

September 1983



84 05 29 039

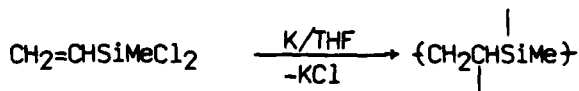
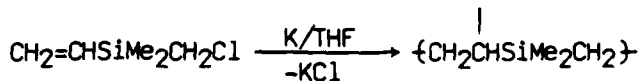
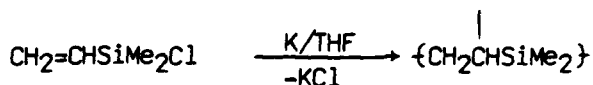
yield after pyrolysis, while a similar polymer prepared with $\text{MeSiHCl}_2/\text{CH}=\text{CHSiMe}_3$ provides a significantly higher ceramic yield. Equivalent results are obtained from copolymers prepared from Me_2SiCl_2 or MeSiHCl_2 and $\text{CH}_2=\text{CHSiMe}_2\text{Cl}$, or from Me_2SiCl_2 or MeSiHCl_2 and $\text{CH}_2=\text{CHSiMe}_2\text{CH}_2\text{Cl}$. In the latter comparison, a 2/1



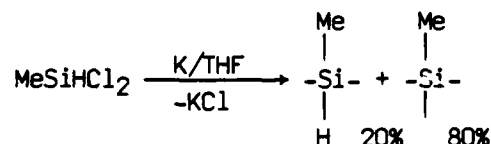
molar ratio of $\text{Me}_2\text{SiCl}_2/\text{CH}_2=\text{CHSiMe}_2\text{CH}_2\text{Cl}$ was used, with a 1.5/1 molar ratio of $\text{MeSiHCl}_2/\text{CH}_2=\text{CHSiMe}_2\text{CH}_2\text{Cl}$.

Since the backbone branching in these polycarbosilane types is responsible for their effective pyrolytic conversion to SiC,¹ it appears that MeSiHCl_2 provides such branching, either by forming trifunctional MeSi^\bullet units during synthesis (with loss of H-groups) or during pyrolysis, by reactions of difunctional $-\text{MeSiH}-$ groups.

It should be noted that the polymeric units derived from $\text{CH}_2=\text{CHSiMe}_2\text{Cl}$ or $\text{CH}_2=\text{CHSiMe}_2\text{CH}_2\text{Cl}$ provide backbone branching at carbon, rather than at silicon, and do not contribute to ceramic yield, while $\text{CH}_2=\text{CHSiMeCl}_2$ provides units with backbone branching at silicon which do contribute to ceramic yield.



Model reactions suggest that the majority of the hydrosilyl groups are lost in the preparative step. Reaction of 2/1 $\text{Me}_3\text{SiCl}/\text{MeSiHCl}_2$ with K/THF provides a low yield of the tetrasilane, $\text{MeSi}(\text{SiMe}_3)_3$,³ as the major volatile product, rather than $\text{MeSiH}(\text{SiMe}_3)_2$. Proton NMR analyses of the MeSiHCl_2 -derived copolymers show that about 20% of the hydrosilyl groups remain, while 80% are



converted to trifunctional branching units. The degree of loss of hydrosilyl functionality may be dependent on the active metal, since lithium causes complete loss,⁴ while sodium retains most of the hydrosilyl groups,⁵ in respective reactions with Me_2SiHCl .



POLYMER PROPERTIES

The soluble solid from dechlorination of 0.85/0.3/1.0 $\text{Me}_3\text{SiCl}/\text{MeSiHCl}_2/\text{CH}_2=\text{CHSiMeCl}_2$ is a colorless resin which thermosets before melting, remaining solid to 300°, at which point pyrolytic degradation commences. TGA Scans of that polymer (Figure I) and the corresponding 0.85/0.3/1.0 $\text{Me}_3\text{SiCl}/\text{Me}_2\text{SiCl}_2/\text{CH}_2=\text{CHSiMeCl}_2$ polymer (Figure II) also demonstrate the higher ceramic yield from the MeSiHCl_2 -derived polymer. The TGA yield figures are somewhat lower than those obtained from bulk pyrolyses, probably due to the higher TGA heating rate and the small TGA sample size.

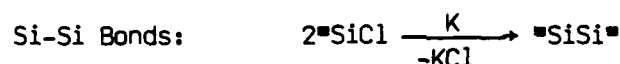
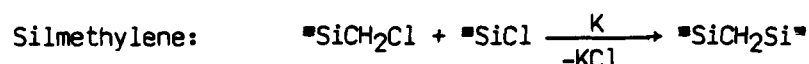
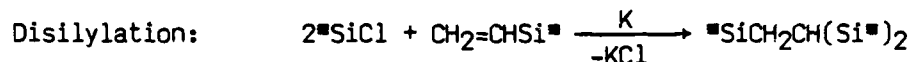
A series of polymers were prepared with relatively lower contents of units derived from MeSiHCl_2 , as in 0.85/0.3/0.3/1.0, 0.85/0.2/0.2/1.0, and 0.85/0.3/0.1/1.0 polymers from $\text{Me}_3\text{SiCl}/\text{Me}_2\text{SiCl}_2/\text{MeSiHCl}_2/\text{CH}_2=\text{CHSiMeCl}_2$ monomer mixtures, to provide materials with better melt properties. The latter two polymers were solids at room temperature, remained fluid after melting to 300°, and were melt-spun to preceramic polycarbosilane fibers.⁶

Fractionation of the 0.85/0.3/1.0 terpolymer from $\text{Me}_3\text{SiCl}/\text{MeSiHCl}_2/\text{CH}_2=\text{CHSiMeCl}_2$ from THF into nonsolvent acetone provided high and low molecular weight fractions in approximately equal amounts.

The high molecular weight fraction provided 53.5% of SiC ceramic composition on pyrolysis, while the low molecular weight fraction yielded 43.2%. Actual molecular weights were not determined, although the polymers are amenable to analysis by gel permeation chromatography.

These polymers do not provide exact elemental analyses⁷ due to oxygen incorporation during hydrolytic termination, loss of hydrogen from SiH groups, and problems in total combustion of preceramic materials.

The major-polymer forming reactions are disilylation of vinyl groups, creation of silylmethylene groups, or formation of silicon-silicon bonds. Model



reactions¹ have shown that formation of Si-C bonds by the first two reactions is generally favored, and instrumental analyses (IR, NMR, IV) are consistent with that fact.

CONCLUSIONS

The use of low levels of MeSiHCl_2 in modifying potassium-derived polycarbosilanes provides significant improvements in yields and qualities of SiC ceramic compositions obtained therefrom. Most of the MeSiHCl_2 reacts to form trifunctional MeSi groups, with about 20% being incorporated as difunctional -MeSiH- units. Residual hydrosilyl groups provide proportionate in situ cross-linking during pyrolysis.

EXPERIMENTAL

All chlorosilanes were freshly distilled before use. THF was reagent grade, dried over Linde 4A molecular sieves. K Metal was purchased as practical grade ingots; all K metal transfers were made under nitrogen in a dry box. All reactions (preparations and pyrolyses) were run under argon or nitrogen. Routine NMR spectra were recorded on a Perkin-Elmer R24A spectrometer - VPC. Analyses were run on a Hewlett-Packard 5840A gas chromatograph. Pyrolyses up to 700° were run in quartz reactors in a Lindberg 54242 tube furnace and those up to 1200° were run in an alumina reactor in a Lindberg 54233 tube furnace. Both furnaces have programmable controllers, which allow attendant-free operation from charging to removal of products. Conversions to SiC compositions were confirmed by x-ray diffraction.

Reaction of 1/1 $\text{MeSiHCl}_2/\text{CH}_2=\text{CHSiMe}_3$ with K/THF

In a 11 3N RB flask were combined 31.6g (0.81 mol) of K metal and 422.9g anhydrous THF. Flask was fitted with mechanical stirrer (stainless steel blade), thermometer, heating mantle, addition funnel, and nitrogen flow valves. Mixture was heated to reflux (66°), melting the K, and addition of a mixture of 38.5g (0.39 mol) of $\text{CH}_2=\text{CHSiMe}_3$ and 44.3g (0.39 mol) of MeSiHCl_2 begun and

completed in 40 min., lowering the reflux temperature to 64°. Heating was resumed at reflux for 5-1/2 hr, followed by cooling on wet ice bath, termination with 6.5g H₂O/48.6g THF solution (dropwise addition), and neutralization with 6.4g conc. HCl. Filtration, trituration, and dissolution of the salts (H₂O) left a trace amount of insoluble solid product. The THF reaction solution and trituration solvent were dried over MgSO₄, filtered, and vacuum distilled, yielding 0.38g up to 35°/1.0 mm plus 24.36g (44%) of heavies. VPC Analysis suggested 20.8g (54%) of CH₂=CHSiMe₃ was unreacted and was removed by stripping. Pyrolysis of the heavies to 1200° in two steps provided 28.5% of SiC composition, showing a weak X-ray diffraction pattern for microcrystalline β-SiC.⁸

A similar copolymer prepared from Me₂SiCl₂/CH₂=CHSiMe₃,^{1,2} provided only 0.3% ceramic on pyrolysis to only 590°.

Reaction of 0.85/0.3/1.0 Me₃SiCl/MeSiHCl₂/CH₂=CHSiMeCl₂ with K/THF

The procedure above was repeated using a 2l flask, 106.4g (2.72 mols) of K metal, 807.1g of tetrahydrofuran, and a mixture of 69.7g (0.64 mol) of Me₃SiCl, 25.9g (0.225 mol) of MeSiHCl₂, and 105.9g (0.75 mol) of CH₂=CHSiMeCl₂. Workup as above yielded 8.7% of insoluble solid product, 9.5% of volatile products, b.p. up to 65°/0.5 mm, and 74.6% of soluble solid product. Pyrolysis of the latter to 1200° in two steps yielded 51.7% of SiC composition having the correct x-ray diffraction pattern for microcrystalline β-SiC.

Analytical:	% C	% H	% Si	% Cl	% O
Calc'd:	48.33	10.22	41.45	0	0
Found:	45.48	9.10	39.63	0.044	5.65
(% O by difference)					

The soluble solid (analysis above) was submitted to Albany International Research Company for spin screening. Under melt spinning conditions, it crosslinked to an insoluble solid.

The procedure was repeated to prepare polymers from 0.85/0.3/0.3/1.0, 0.85/0.2/0.2/1.0, and 0.85/0.3/0.1/1.0 ratios of Me₃SiCl/Me₂SiCl₂/MeSiHCl₂/CH₂=CHSiMeCl₂. The latter two polymers were successfully melt-spun to preceramic fibers. The respective bulk pyrolysis yields of SiC ceramic compositions were 41.6%, 40.8%, and 35.5%.

REFERENCES

- 1a. C. L. Schilling, Jr., J. P. Wesson, and T. C. Williams, Am. Ceram. Soc. Bull. 62, 912 (1983).
- b. J. Poly. Sci., Polym. Symposia, in press.
- c. ONR Technical Report TR-80-1; Chem. Abstr., 95, 170175q (1981).

Reference 1b contains a review of organosilicon polymer routes to SiC ceramics.

2. O. M. Nefedov, et. al., Proc. Acad. Sci. USSR, 154, 76 (1964).
3. W. H. Atwell and D. R. Weyenberg, J. Organometal. Chem., 5, 594 (1966).
4. W. Peterson and B. Arkles, U.S. Patent 4,276,424; June 30, 1981.
5. P. Gerval et. al., Bull. Soc. Chim. France, 1974, p. 1548.
6. Spinning tests performed by Glenn Howland, Albany International Research Co., Dedham, Mass.
7. Elemental analyses by Galbraith Laboratories, Knoxville, Tenn.
8. S. Yajima, et. al., Nature, 279, 706 (1979).

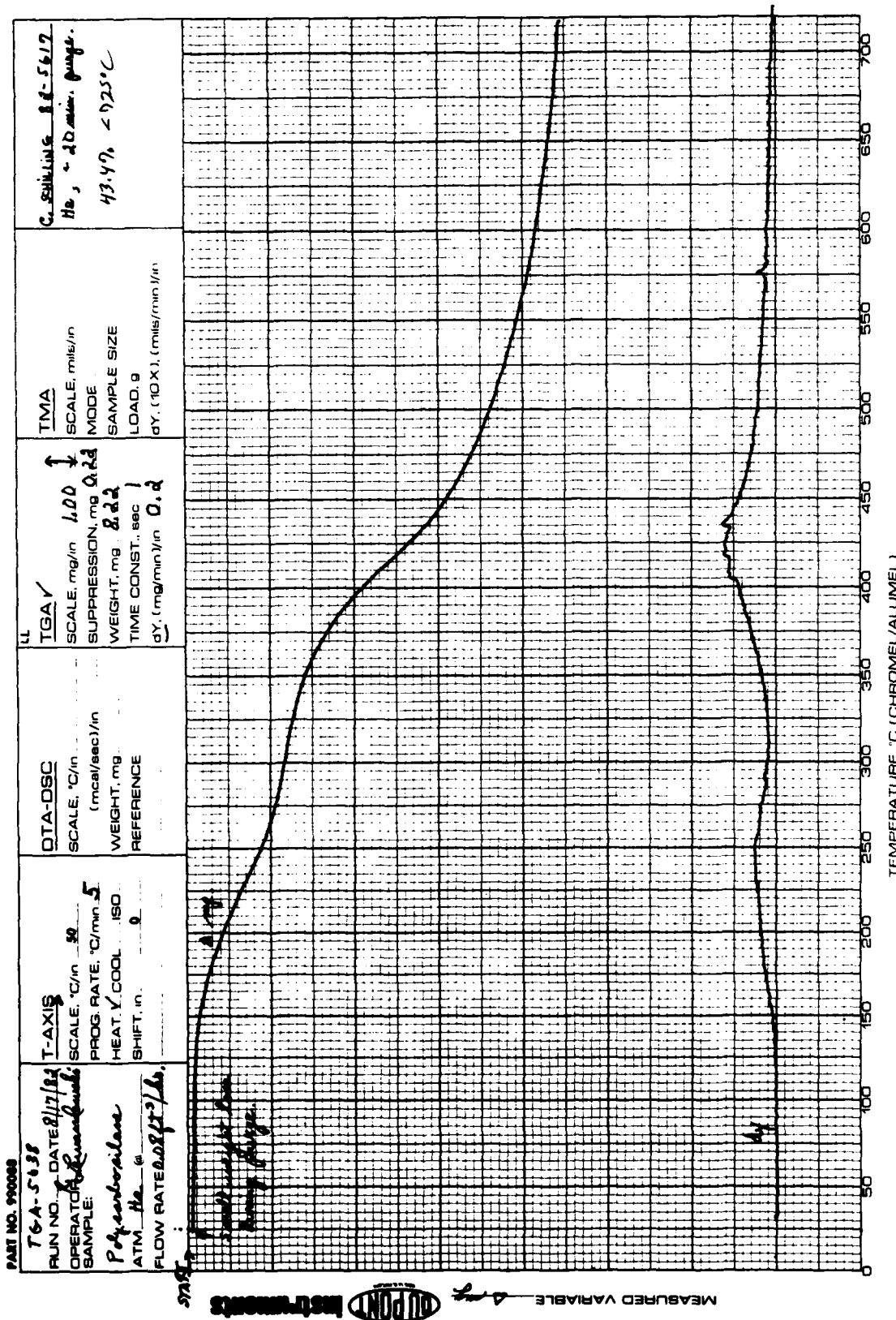
FIGURES

- Figure I TGA of Terpolymer from
0.85/0.3/1.0 Me₃SiCl/ MeSiHCl₂/CH₂=CHSiMeCl₂
- Figure II TGA Scan of Terpolymer from
0.85/0.3/1.0 Me₃SiCl/Me₂SiCl₂/CH₂=CHSiMeCl₂

ORGANOSILANE POLYMERS, V

Figure 1

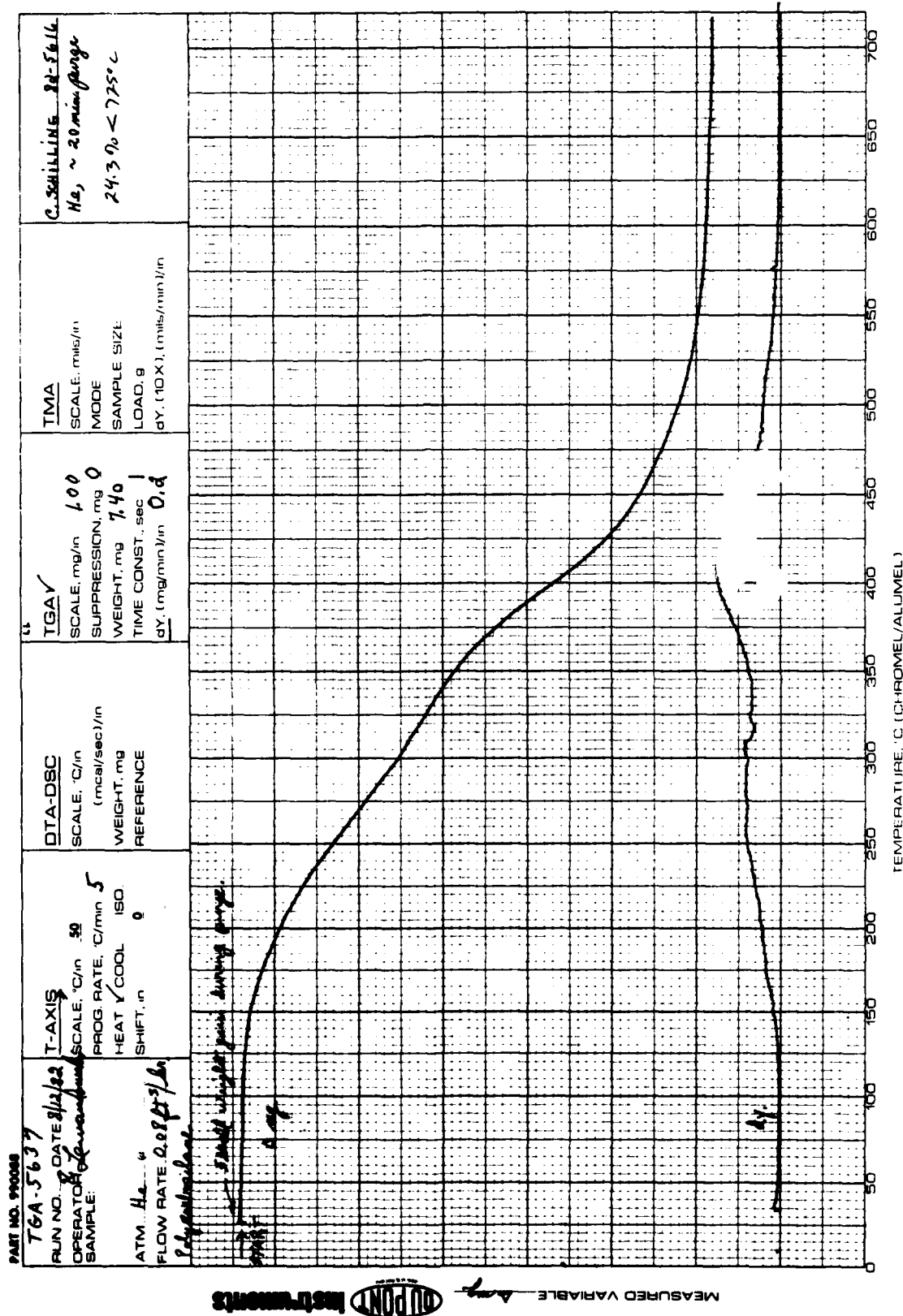
TGA Scan of Terpolymer from 0.85/0.3 /1.0
Me₃SiCl/MeSiHCl₂/CH₂=CHSiMeCl₂



ORGANOSILANE POLYMERS, V

Figure II

TGA Scan of Terpolymer from 0.85/0.3/1.0
 $\text{Me}_3\text{SiCl}/\text{Me}_2\text{SiCl}_2/\text{CH}_2=\text{CHSiMeCl}_2$



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Weapons Center Attn: Dr. A. B. Amster Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. Vincent Schaper DTNSRDC Code 2830 Annapolis, Maryland 21402	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1	Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

TECHNICAL REPORT DISTRIBUTION LIST, 356B

Dr. C. L. Schilling
Union Carbide Corporation
Chemical and Plastics
Tarrytown Technical Center
Tarrytown, New York

Dr. A. G. MacDiarmid
Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19174

Dr. E. Fischer, Code 2853
Naval Ship Research and
Development Center
Annapolis, Maryland 21402

Dr. H. Allcock
Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802

Dr. M. Kenney
Department of Chemistry
Case Western University
Cleveland, Ohio 44106

Dr. R. Lenz
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

Dr. M. David Curtis
Department of Chemistry
University of Michigan
Ann Arbor, Michigan 48105

NASA-Lewis Research Center
Attn: Dr. T. T. Serafini, MS 49-1
21000 Brookpark Road
Cleveland, Ohio 44135

Dr. J. Griffith
Naval Research Laboratory
Chemistry Section, Code 6120
Washington, D.C. 20375

Professor G. Wnek
Department of Materials Science
and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. R. Soulen
Contract Research Department
Pennwalt Corporation
900 First Avenue
King of Prussia, Pennsylvania 19406

Dr. G. Goodman
Globe-Union Incorporated
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201

Dr. Martin H. Kaufman
Code 38506
Naval Weapons Center
China Lake, California 93555

Dr. C. Allen
Department of Chemistry
University of Vermont
Burlington, Vermont 05401

Professor R. Drago
Department of Chemistry
University of Florida
Gainesville, Florida 32611

Dr. D. L. Venezky
Code 6130
Naval Research Laboratory
Washington, D.C. 20375

Professor T. Katz
Department of Chemistry
Columbia University
New York, New York 10027

Professor James Chien
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

Professor J. Salamone
Department of Chemistry
University of Lowell
Lowell, Massachusetts 01854

Dr. S. Cooper
Department of Chemistry
University of Wisconsin
750 University Avenue
Madison, Wisconsin 53706

TECHNICAL REPORT DISTRIBUTION LIST, 356B

Professor D. Grubb
Department of Materials Science
and Engineering
Cornell University
Ithaca, New York 14853

Professor T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Professor C. Chung
Department of Materials Engineering
Rensselaer Polytechnic Institute
Troy, New York 12181

Professor Malcolm B. Polk
Department of Chemistry
Atlanta University
Atlanta, Georgia 30314

Dr. D. B. Cotts
SRI International
333 Ravenswood Avenue
Menlo Park, California 94205

Dr. Kurt Baum
Fluorochem, Inc.
680 S. Ayon Avenue
Azusa, California 91702

Professor H. Hall
Department of Chemistry
University of Arizona
Tucson, Arizona 85721

Professor G. Whitesides
Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

Professor H. Ishida
Department of Macromolecular Science
Case Western University
Cleveland, Ohio 44106

Dr. K. Paciorek
Ultrasystems, Inc.
P.O. Box 19605
Irvine, California 92715

Professor D. Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. G. Bryan Street
IBM Research Laboratory, K32/281
San Jose, California 95193

CAPT J. J. Auburn, USNR
AT&T Bell Laboratories
Room 6F-211
600 Mountain Avenue
Murray Hill, New Jersey 07974
A